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Investigation on intermolecular interaction between two solutes where one solute occurs in two states

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ABSTRACT

The spectral behavior of a pair of 2D asynchronous spectra generated by using the double asynchronous orthogonal sample design (DAOSD) approach on a chemical system is investigated. Two solutes (P and Q) are dissolved in the solution and intermolecular interaction between P and Q is characterized. In this particular system, P occurs in two exchangeable states when it is dissolved in the solutions. Results on mathematical analysis and computer simulation demonstrated that interference unrelated to the intermolecular interaction can be completely removed. Hence the resultant 2D asynchronous spectra generated by using the DAOSD approach can reflect intermolecular interaction reliably. Moreover, properties of cross peaks in different regions of the pair of asynchronous spectra are discussed. In our previous works, cross peaks generated by using the DAOSD and relevant techniques reflect variations on peak position, bandwidth or absorptivity of the characteristic peaks of solutes caused by intermolecular interaction. However, we find that cross peak can still be produced even if intermolecular interaction do not bring about any changes on the characteristic peaks of solutes. Mathematical analysis demonstrates that cross peaks are related to the variations of chemical systems caused by intermolecular interaction at a network level.

1. Introduction

Two-dimensional correlation spectroscopy is a powerful spectroscopic technique. It transforms a set of spectral data obtained sequentially under some forms of perturbation on the sample into a correlation intensity plot on a spectral plane defined by two independent spectral variable axes. Since proposed by Noda in the late 1980s [1,2], 2D correlation spectroscopy has attracted extensive interests and a large amount of research work has been accumulated in the literature [3–15]. One of the most important applications on 2D correlation spectroscopy is to characterize intermolecular interaction in a variety of chemical systems [16–33].

In our previous work, we have developed orthogonal sample design (OSD) [34–39] scheme to characterize intermolecular interactions between two solutes dissolved in the same solutions. The OSD approach is to design concentrations for the two solutes in a series of solutions. The purpose of the approach is that spectral signals irrelevant to the intermolecular interactions can be completely removed via multiplication of two vectors that are orthogonal to each other. As a result, intermolecular interaction, which is manifested as systematic deviation from the Beer-Lambert's Law, appears as cross peaks in the resultant 2D synchronous spectra. Based on the concept of orthogonality, we have introduced asynchronous orthogonal sample design (AOSD) [40–42], double orthogonal sample design (DOSD) [43] and double asynchronous orthogonal sample design (DAOSD) [44–51], asynchronous spectrum with auxiliary cross peak (ASAP) [52] and other approaches [53,54] to enhance the ability of 2D correlation spectroscopy to

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reveal spectral variations on the characteristic peaks of solutes caused by intermolecular interactions.

When intermolecular interaction between two solutes is investigated by using the OSD and relevant approaches, we assume that each of the solutes should be in a single state when it is dissolved in the solution. However, many substances in the real world may occur in more than one state when they are dissolved in a solution. For example, equilibrium may set up between two distinct conformers as a solute is dissolved. In many cases, the solute may act as a weak base so that it may exist in different protonation states. Additionally, some solute molecules may undergo keto-enol tautomerism. In the above instances, additional complexity will be brought about when a second solute is introduced and intermolecular interactions occur between the first solute in different forms and the second solute. Understanding on the nature of the interactions in these systems are very important to enhance our research on molecular self-assembly and molecular catalysis. Upon to now, the use of OSD and relevant approaches on these multi-state systems has not been explored.

The DAOSD approach, developed in our previous work, is a powerful spectral analysis technique to reveal subtle spectral changes caused by intermolecular interaction. The full description of the DAOSD approach can be found in our previous work [44] and a brief introduction is provided in the first part of supporting information. In this paper, mathematical analysis and computer simulation are carried out to study the spectral behaviors of a pair of 2D asynchronous spectra generated by using the DAOSD approach.

2. Experimental

2.1. Description of the model system

The chemical system studied here is a series of solutions where two solutes (denoted as P and Q) are dissolved. In this system, P exists in two distinct inter-conversable states (denoted as P_1 and P_2, respectively). The inter-conversion is specified in terms of Eq. (1) and the equilibrium constant is K_0.

$$P_1 \xleftrightarrow{K_0} P_2 \tag{1}$$

Under intermolecular interaction between P_1 and Q, part of P_1 undergoes subtle structure variation and converts into U_1 and part of Q converts into V_1. Similarly, part of P_2 converts into U_2 and part of Q converts into V_2 due to the interaction between P_2 and Q. These interactions could be specified in terms of Eq. (2) and Eq. (3) where the corresponding equilibrium constants are K_1 and K_2, respectively.

$$P_1 + Q \xleftrightarrow{K_1} U_1 + V_1 \tag{2}$$

$$P_2 + Q \xleftrightarrow{K_2} U_2 + V_2 \tag{3}$$

The spectral function of each substance (P_1, P_2, Q, U_1, U_2, V_1 and V_2) possesses only one characteristic peak. The peak for each chemical species is represented by a Gaussian function as shown in Eq. (4).

$$f_j(x) = \varepsilon_j {*} e^{-(\ln 2){*}\left[\frac{(x-x_j)^2}{W_j^2}\right]} = \varepsilon_j g_j(x) \tag{4}$$

where j is the index of the seven chemical species, i.e., P_1, P_2, Q, U_1, U_2, V_1 and V_2; ε_j, x_j, and W_j are the corresponding molar absorptivity, peak position and bandwidth (half-width at half-height, HWHH) of the characteristic band of the jth chemical species; $g_j(x)$ is the peak shape function that is relevant to peak position and bandwidth.

To reflect the spectral behaviors of the 2D asynchronous spectra generated by using the DAOSD approach clearly, we assume that the characteristic peaks of P_1, P_2 and Q are not overlapped with one another. However, the peak of P_1 is highly overlapped with that of U_1 since interaction is quite weak and only induces subtle spectral variation. Similarly, the peak of P_2 is highly overlapped with that of U_2 and the peak of Q is overlapped severely with the peaks of V_1 and V_2. The peak parameters of P_1, P_2, Q, U_1, V_I, U_2 and V_2 are listed in Table 1. The subtle variations of peak parameters (i.e., absorptivity, bandwidth and peak position) of P_1, P_2 and Q are defined in Table 2.

2.2. construction of a pair of 2D asynchronous spectra based on the DAOSD approach

According to the DAOSD approach, two groups of solutions are simulated. The initial concentrations of P and Q of the two groups of solutions are listed in Table 3.

For the ith solution, the simulated 1D spectrum is constructed by using Eq. (5) according to the Beer-Lambert's Law.

$$A^i(x) = C_{P_1}^{i(eq)} l f_{P_1}(x) + C_{P_2}^{i(eq)} l f_{P_2}(x) + C_{Q}^{i(eq)} l f_{Q}(x) + C_{U_1}^{i(eq)} l f_{U_1}(x) + C_{U_2}^{i(eq)} l f_{U_2}(x) + C_{V_1}^{i(eq)} l f_{V_1}(x) + C_{V_2}^{i(eq)} l f_{V_2}(x) \tag{5}$$

where $f_{P_1}(x), f_{P_2}(x), f_Q(x), f_{U_1}(x), f_{U_2}(x), f_{V_1}(x)$ and $f_{V_2}(x)$ are spectral functions of P_1, P_2, Q, U_1, U_2, V_1 and V_2; l is the path-length and is set as 1 for convenience; $C_{P_1}^{i(eq)}, C_{P_2}^{i(eq)}, C_{Q}^{i(eq)}, C_{U_1}^{i(eq)}, C_{U_2}^{i(eq)}, C_{V_1}^{i(eq)}$ and $C_{V_2}^{i(eq)}$ are equilibrium concentrations of P_1, P_2, Q, U_1, U_2, V_1 and V_2. The method of obtaining the equilibrium concentrations of the above substances is discussed in second part of supporting information.

To construct 2D asynchronous spectra, dynamic spectrum of the ith solution is generated by using Eq. (6)

$$\widetilde{A}^i(x) = \widetilde{C}_{P_1}^{i(eq)} f_{P_1}(x) + \widetilde{C}_{P_2}^{i(eq)} f_{P_2}(x) + \widetilde{C}_{Q}^{i(eq)} f_{Q}(x) + \widetilde{C}_{U_1}^{i(eq)} f_{U_1}(x) + \widetilde{C}_{U_2}^{i(eq)} f_{U_2}(x) + \widetilde{C}_{V_1}^{i(eq)} f_{V_1}(x) + \widetilde{C}_{V_2}^{i(eq)} f_{V_2}(x) \tag{6}$$

where

$$\widetilde{C}_{P_1}^{i(eq)} = C_{P_1}^{i(eq)} - C_{P_1}^{eq(av)} \tag{7a}$$

$$\widetilde{C}_{P_2}^{i(eq)} = C_{P_2}^{i(eq)} - C_{P_2}^{eq(av)} \tag{7b}$$

$$\widetilde{C}_{Q}^{i(eq)} = C_{Q}^{i(eq)} - C_{Q}^{eq(av)} \tag{7c}$$

$$\widetilde{C}_{U_1}^{i(eq)} = C_{U_1}^{i(eq)} - C_{U_1}^{eq(av)} \tag{7d}$$

Table 1
Spectral parameters of P_1, P_2, Q, U_1, V_1, U_2 and V_2 in the model system when interaction occurs between P and Q.

Spectral variable	Peak position (nm)	Bandwidth (nm)	Absorptivity
P_1	100	20	1.0
P_2	300	20	1.0
Q	500	20	1.0
U_1	105	20	1.0
V_1	510	20	1.0
U_2	295	20	1.0
V_2	490	20	1.0